

Analysis of cubic and orthorhombic C₃A hydration in presence of gypsum and lime

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Abstract Field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD) have been used to study the microstructural changes and phase development that take place during the hydration of cubic (pure) and orthorhombic (Na-doped) tricalcium aluminate (C₃A) and gypsum in the absence and presence of lime. The results demonstrate that important differences occur in the hydration of each C₃A polymorph and gypsum when no lime is added; orthorhombic C₃A reacts faster with gypsum than the cubic phase, forming longer ettringite needles; however, the presence of lime slows down the formation of ettringite in the orthorhombic sample. Additional rheometric tests showed the possible effects on the setting time in these cementitious mixes.

Introduction

Cement chemistry uses the term “hydration” to denote the changes that occur when the anhydrous cement, or one of

its phases (the so-called clinker phases), are mixed with water. This involves a complex group of reactions that cause changes in the chemical and physico-mechanical properties of the system, particularly in the setting and hardening of the mix [1]. The hydration process is sensitive to many factors, among which clinker composition is of special relevance because it controls the kinetics of cement hydration [2]. The knowledge of the hydration behavior of a pure phase and its interaction with other phases form the basis of the interpretation of the complex reactions, which occur in the Portland cement hydration under various conditions.

The reaction of tricalcium aluminate (C₃A) with water is instantaneous. Crystalline hydrates, such as C₃AH₆, C₄AH₁₉, and C₂AH₈, form quickly, generating large amounts of heat [3 and references therein]. This happens even in the presence of retarders, as observed by means of ²⁷Al MAS NMR [4]. To slow down the hydration reaction, calcium sulfate is added to the mix, which causes ettringite to form. Ettringite is a calcium sulpho-aluminate (C₆A \overline{S} ₆H₃₂) that forms during the first stages of hydration and subsequently develops a three-dimensional nanocrystal network, which ultimately leads to setting and hardening of the cement paste. If hydration of C₃A in cement is not controlled, setting occurs very rapidly and the resulting mix cannot be used for most construction applications because of its high viscosity and low workability.

Industrial clinkers contain minor elements such as Na₂O, K₂O, SiO₂, Fe₂O₃, SO₃, and Cl[−], coming from raw materials, fuel, and the lining of the kilns [5, 6]. These alkalis can be incorporated into a number of phases in the clinker, and often Na₂O is normally taken up by the C₃A [7]. When C₃A is synthesized in the presence of these elements, it causes changes in its crystal lattice, and the formation of the other phases occurs. There are several

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solid solutions of general formula $\text{Na}_{2x}\text{Ca}_{3-x}\text{Al}_2\text{O}_6$, such as cubic, monoclinic, orthorhombic, and tetragonal [8–10], but in cements, the cubic or orthorhombic C_3A are found alone or in combination [11].

Numerous studies have been conducted to quantify the influence of these polymorphs (cubic and orthorhombic) on the mechanisms of cement hydration, such as those by Boikova and Domansky [10]; Regourd et al. [12]; Odler and Wonnemann [13]; Massazza and Daimon [6]; Samet and Sarkar [14]; and Stephan and Wistuba [15]. Despite these studies, however, a consensus has not been reached, and a sizeable knowledge gap still exists concerning the specific characteristics of each polymorph, having a marked effect on their reactivity.

Although C_3A is a small component of most clinkers (commonly 4–10 wt%), the content of this aluminate can reach values exceeding 10 wt% in white Portland cement (WPC) [16]. The high concentration of C_3A in the composition of WPC affects the setting time of this cement, resulting in a normally shorter setting time compared to ordinary Portland cement (OPC) [17]. Moreover, these high levels must also be taken into account regarding long-term durability issues, as the reactivity of calcium aluminate with sulfate-bearing solutions make high- C_3A cements especially prone to develop a series of deleterious reactions known generically as “sulfate attack”. Therefore, detailed microstructural and mineralogical studies of the hydration behavior of C_3A polymorphs are of major importance in understanding the complexity of the setting mechanisms of cements with relatively high contents of tricalcium aluminate. To better understand how the presence of gypsum and lime affect the hydration of cubic and orthorhombic C_3A , this study conducted a detailed FE-SEM, XRD, and rheological study of the hydration behavior of synthetic cubic and orthorhombic C_3A in the presence of gypsum, with and without the addition of lime.

Experimental section

Materials

Samples of tricalcium aluminate (C_3A), orthorhombic and cubic, were obtained from Construction Technology Laboratories, Inc., located in Skokie, Illinois. The pure

compounds of orthorhombic and cubic C_3A were synthesized in the laboratory by heating a stoichiometric blend of reagent grade CaCO_3 and alumina (Al_2O_3) in an electric furnace at 1,400 °C for 1 h, followed by quenching in air. The orthorhombic C_3A is composed of $\text{Na}_2\text{Ca}_8\text{Al}_6\text{O}_{18}$; to synthesize it, the reagent grade Na_2CO_3 was also used as a raw material. After synthesizing, each material was ground in a ceramic mill to 325 meshes. The powders were characterized by means of thermo-gravimetric analysis, X-ray fluorescence, XRD, and laser granulometry methods. The gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and lime (CaO) used in this study were provided by *Fisher Scientist*, located in Pittsburgh, Pennsylvania.

Methods

For the FE-SEM and XRD analysis, the samples were hand mixed for 2 min and then stored at 100% RH, and covered with a plastic film until they were studied 7 or 14 days later. The amount of each compound (gypsum and both C_3A) was stoichiometrically calculated based on the quantity necessary to form ettringite, which resulted in a 1:1.9 ratio (C_3A :gypsum); the water content was 0.6 (water-to-solid materials ratio—w/s). Ten percent lime with respect to C_3A amount was added in the pastes to observe how increasing the system alkalinity affects ettringite formation. Table 1 shows how the mixes proportions were set in the experiments.

Selected samples of these pastes were sputtered with gold and investigated with a Hitachi S-5000 FE-SEM.

X-ray investigations were carried out with a Phillips XPert MPD PW3373/00 diffractometer operated at an accelerating voltage of 40 keV on a $\text{CuK}\alpha$ anode, irradiation intensity of 40 mA, and 40° scans in steps of 0.02°/s.

The evolution of early hydration of additional mixes prepared with the same material ratios was studied with a Haake RheoStress 600 rheometer (RT) with plate–plate configuration, operating in controlled strain mode. The rotating plate was 8 mm in diameter, and the side in contact with the sample was grooved in order to prevent possible slippage. The samples were hand mixed for 2 min before placing them on the fixed lower plate. The upper plate was then lowered down to a final thickness of the sample of 2 mm. The excess of sample was removed from the lower plate. Next, a shear rate of 600 s^{-1} was applied

Table 1 Mix proportion

C_3A :gypsum ratio	C_3A form	C_3A (g)	CH (g)	Gypsum (g)	Water (g)	w/s	Analysis by means of
1:1.9	Cubic	2.5	–	4.78	4.3	0.6	FE-SEM, DRX, RT
1:1.9		2.5	0.25	4.78	4.5	0.6	FE-SEM, DRX
1:1.9	Orthorhombic	2.5	–	4.78	4.3	0.6	FE-SEM, DRX, RT
1:1.9		2.5	0.25	4.78	4.5	0.6	FE-SEM, DRX

for 30 s; then during the next 60 s the samples remained still; and, finally, a sweep of strains was applied at a fixed frequency of 5 rad/s. The total time elapsed for each test was 14 min and started immediately when the hydration began. The temperature on the fixed plate was kept at 20 ± 1 °C. This configuration was based on Nachbaur et al. [18], Schmidt and Schlegel [19], and Sun et al. [20].

Results

Microscopic examination and XRD measurements

The morphological study of ettringite formation in the systems of cubic C_3A , gypsum, and lime was performed with a FE-SEM and XRD, each system was presented separated to better understand the results.

Hydration of cubic C_3A and gypsum

Figure 1 presents FE-SEM micrographs of a paste consisting of cubic C_3A and gypsum, hydrated for 7 and 14 days, with a $w/s = 0.6$. The pictures show that at

14 days, the sample still contains tricalcium aluminate and gypsum, also confirmed by XRD analysis (Fig. 2b). Ettringite, forming stubby crystals of up to a few hundreds of nanometers in length, is clearly evident in association with C_3A grains. After 14 days, the crystals are longer (typically ≥ 1 μm) and more abundant. Phase confirmation of ettringite is obtained from its low-angle X-ray tag ($d\text{-spacing} = 9.8$ Å) that allows it to be easily distinguished from residual gypsum (7.7 Å). This paste after 7 days remains wet in the sample holder.

In a similar study, Bishop et al. [4] found that the ettringite rods generally range from 1 to 2 μm in length and are about 10–20 nm wide when grown in situ from pastes of cubic C_3A and gypsum.

Hydration of cubic C_3A + gypsum + 10% lime

Figure 3 shows the FE-SEM micrographs of a paste with cubic C_3A , lime, and gypsum hydrated for 7 and 14 days. After 14 days, gypsum and C_3A are still present, also confirmed by XRD analysis (Fig. 4b). The sample presents the same behavior as the mix without lime. In this micrograph, the ettringite is evident close to the particles of C_3A

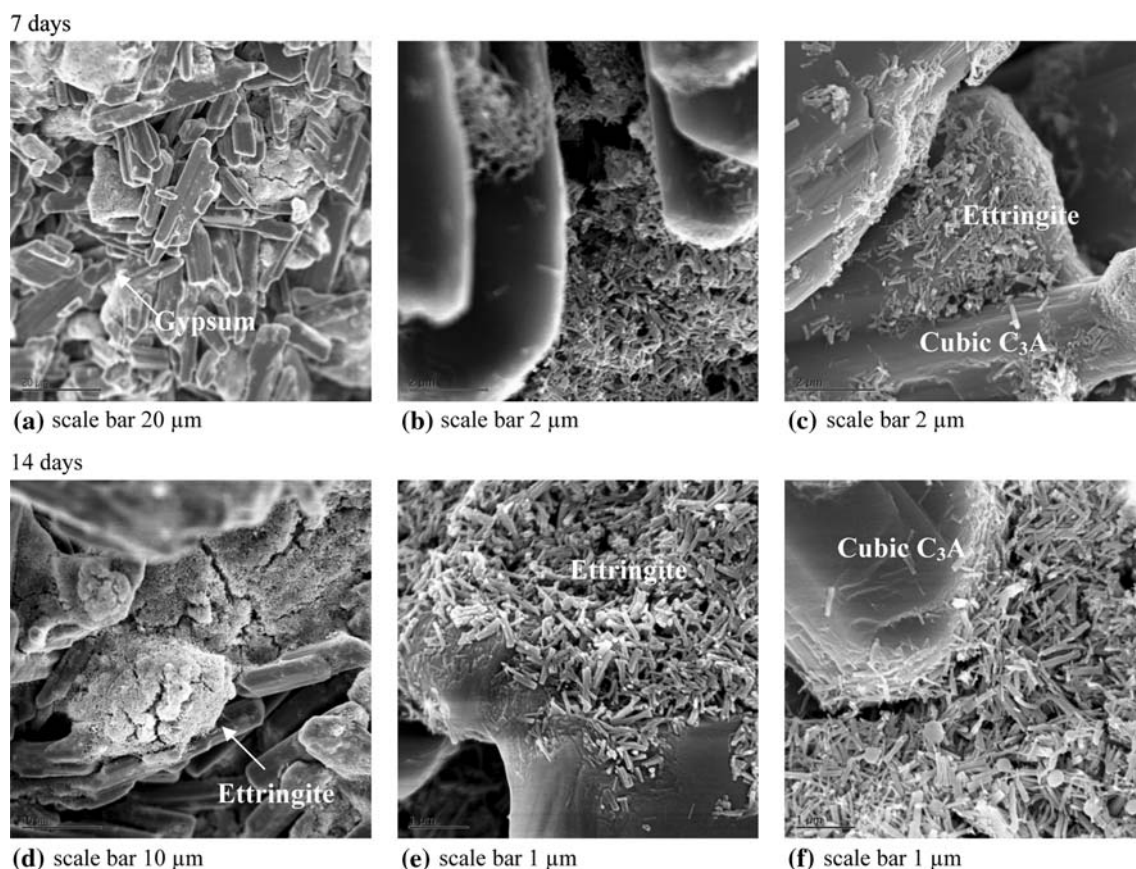


Fig. 1 SEM pictures of ettringite formation from a cubic C_3A + gypsum + H_2O mixture, at 7 and 14 days. $w/s = 0.6$

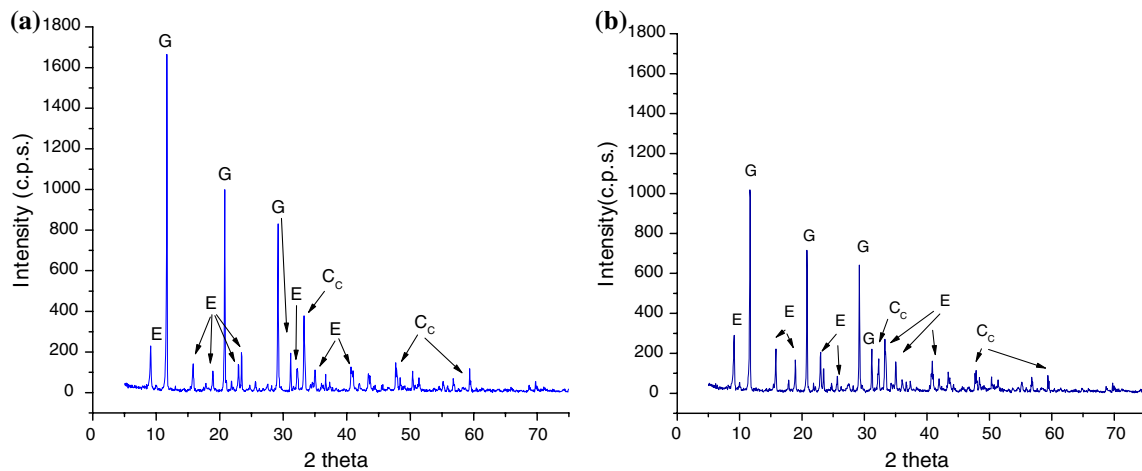


Fig. 2 XRD patterns recorded from the hydrated pastes at 7 days (a) and 14 days (b). Key: E = ettringite; G = gypsum; C_c = cubic C₃A

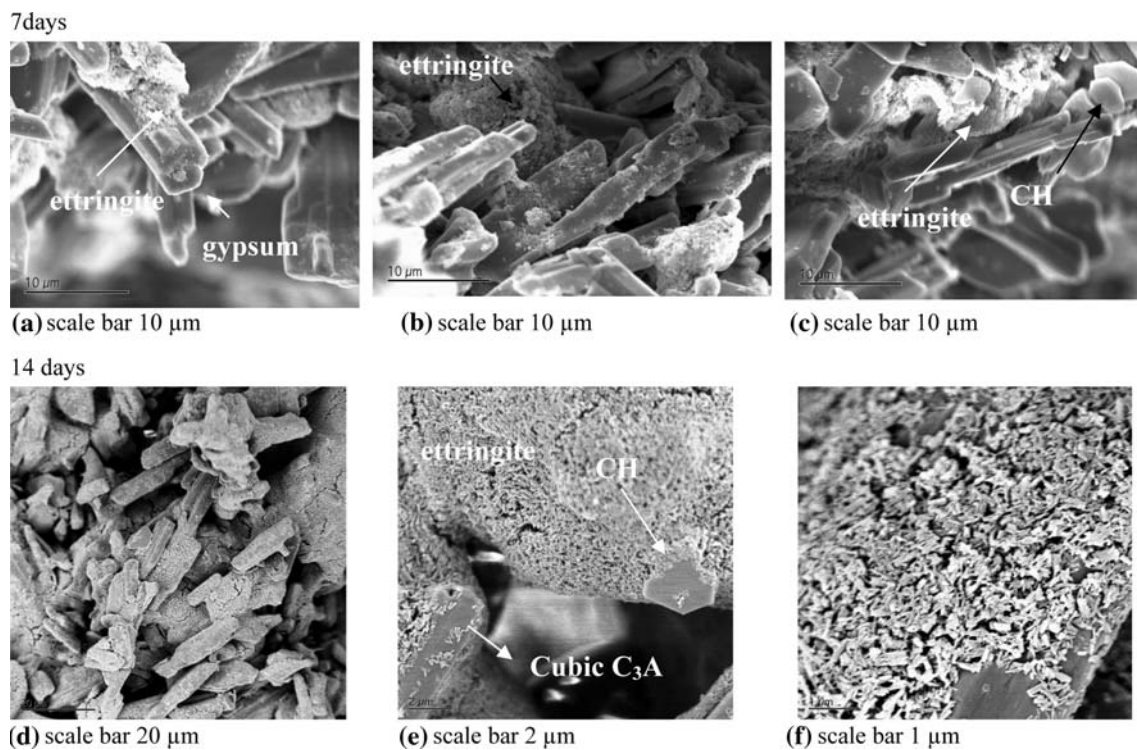


Fig. 3 SEM pictures of ettringite formation from a cubic C₃A + gypsum + 10% lime + H₂O mixture, at 7 and 14 days. *w/s* = 0.6

and gypsum, and formation of portlandite (CH) is also clear. The crystal size of ettringite is, again, of a few hundreds of nm in length.

Hydration of orthorhombic C₃A + gypsum

Figure 5 shows the appearance of the pastes after 7 days. The paste with orthorhombic C₃A is dry and shows little expansion when compared to the paste with cubic C₃A in the same mix proportion. Figure 6 presents the FE-SEM micrographs of pastes of orthorhombic C₃A and gypsum

hydrated for 7 and 14 days. The images indicate that at 7 days, the samples apparently contain no residual gypsum, but peaks of small intensity of gypsum are detected in XRD (Fig. 7a). These FE-SEM images demonstrate that orthorhombic C₃A reacts at a faster rate when compared with the cubic C₃A pastes in the same proportion, because all the gypsum was consumed by 7 days of hydration. The ettringite formation can be seen by the dissolution of C₃A and consumption of all gypsum on the sample after 14 days (Fig. 7b). When compared to pastes with cubic C₃A, in presence and absence of lime, the crystal size is longer,

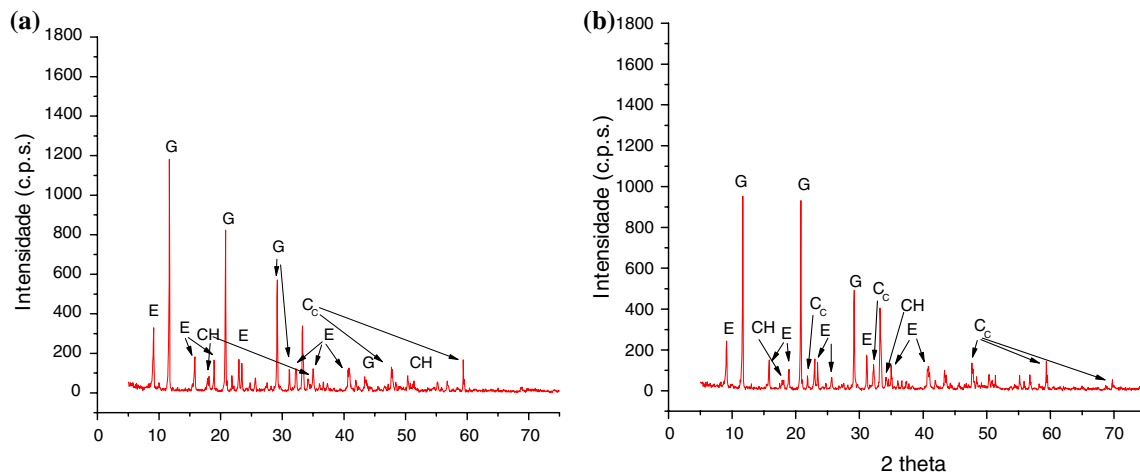
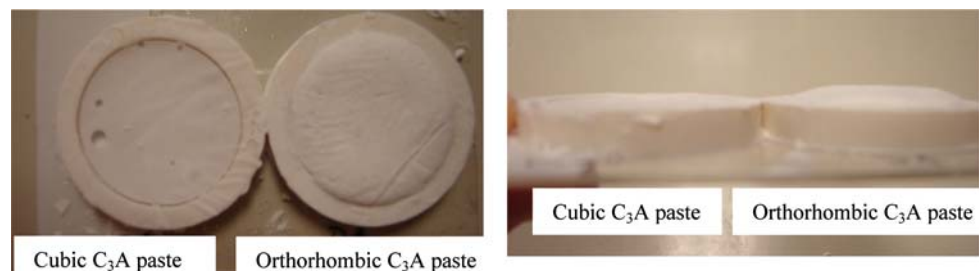


Fig. 4 XRD patterns recorded from the hydrated pastes at 7 days (a) and 14 days (b). Key: E = ettringite; G = gypsum; C_c = cubic C₃A, CH = calcium hydroxide

Fig. 5 Aspect of the cubic and orthorhombic C₃A + gypsum in the sample holder at 7 days of hydration



ranging between 1 and 4 μm in length at both ages, 7 and 14 days.

Hydration of orthorhombic C₃A + gypsum + 10% lime

Figure 8 presents the FE-SEM micrographs of a paste of orthorhombic C₃A, lime, and gypsum hydrated for 7 and 14 days. The XRD patterns show that at 14 days (Fig. 9b), the sample still contains gypsum and C₃A. The behavior of orthorhombic C₃A + gypsum in presence of 10% of lime resulted in a retardation of ettringite formation. The formation of CH occurred, and the crystals size of ettringite was smaller (1 μm in length) when compared to the paste of orthorhombic C₃A with no lime.

Oscillatory rheometric measurement

Figure 10 shows the evolution of the storage modulus (G') of freshly prepared mixes of the two polymorphs of C₃A hydrating in the presence of gypsum. The stiffness was higher in the orthorhombic C₃A mix from the beginning of the test and, most importantly, increased at a higher rate than that of the cubic C₃A-based mix during the very first minutes of the hydration. Thus, an average increase of 158 Pa/s was measured from the former, whereas 97 Pa/s was obtained from the latter. These results may well

suggest that a faster hydration of the orthorhombic C₃A is evidenced from the very early stage of the process and, as a consequence, the mix tends to set earlier in this case. Likewise, this is in accordance with the results from FE-SEM and XRD obtained at much later ages.

Discussion

The images and the XRD patterns demonstrate that the pastes containing orthorhombic C₃A reacted at a faster rate. By the seventh day of hydration, all the gypsum had been consumed, and by 14 days, the XRD diffraction showed only peaks of ettringite on the orthorhombic C₃A paste, whereas after 14 days, traces of gypsum and cubic C₃A remain in the paste with this aluminate.

Interestingly, the ettringite formation appeared to be retarded in both C₃A pastes that contained lime, being much more retarded in the orthorhombic sample when compared with the correlate sample with no lime. Also the size of ettringite crystals was smaller when compared with those obtained from mixes without lime.

These observations may be explained in terms of the pH. Goetz-Neunhoeffer et al. [2] stated that depending on pH, two extreme crystal morphologies of ettringite could be

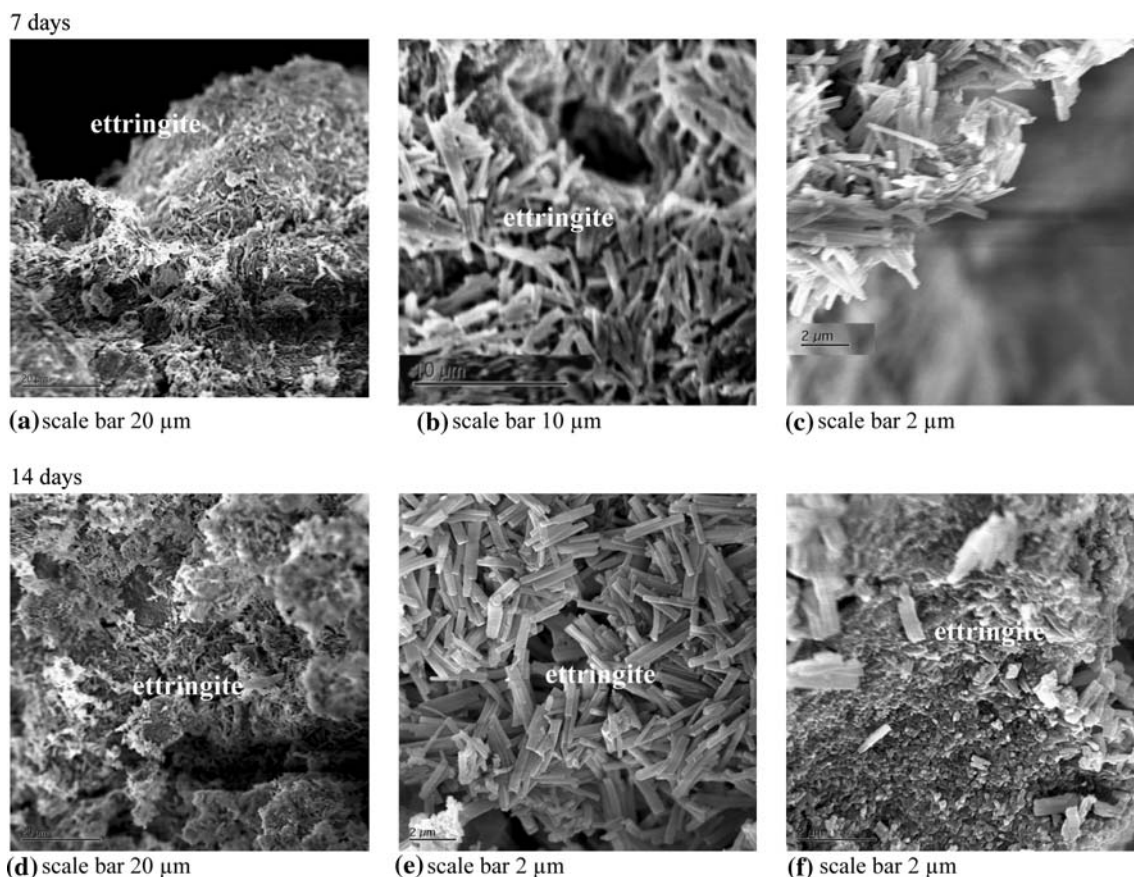


Fig. 6 SEM pictures of ettringite formation from a orthorhombic C_3A + gypsum + H_2O mixture, at 7 and 14 days. $w/s = 0.6$

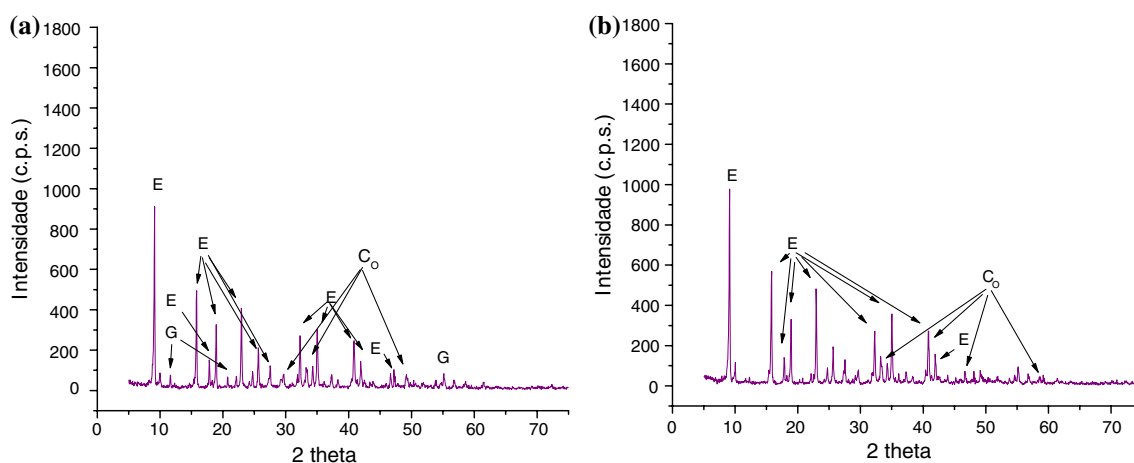


Fig. 7 XRD patterns recorded from the hydrated pastes at 7 days (a) and 14 days (b). Key: E = ettringite; G = gypsum; C_o = orthorhombic C_3A

determined. When the pH is 9.5 in solution, the precipitated ettringite crystals exhibit a very thin extremely acicular shape and are grown together in the direction of c -axis. The hexagonal prisms were up to 110 Å in length. Changing the pH to 12.5, by addition of sodium hydroxide, led to more prismatic hexagonal crystals, which achieved lengths up to 20 Å in direction of c -axis.

In this research, the addition of lime resulted in the formation of $Ca(OH)_2$, which led to an increase in the pH. The presence of $Ca(OH)_2$ changes considerably the course of hydration of C_3A , as this compound reduces the solubility of Al, thus increasing the pH [6, 21].

Based on these results, when the alkaline level is increased because of an increase in the amount of alkalis in

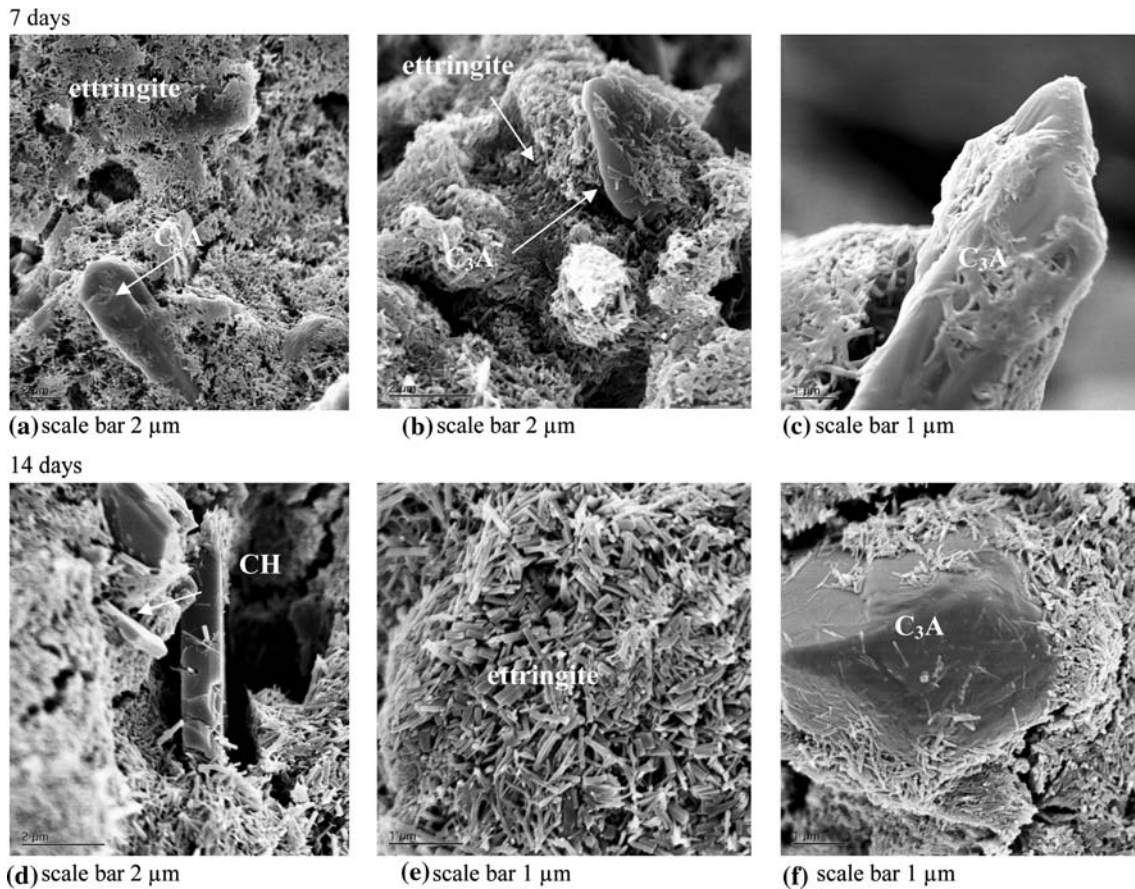


Fig. 8 SEM pictures of ettringite formation from an orthorhombic C_3A + gypsum + lime + H_2O mixture, at 7 and 14 days. $w/s = 0.6$

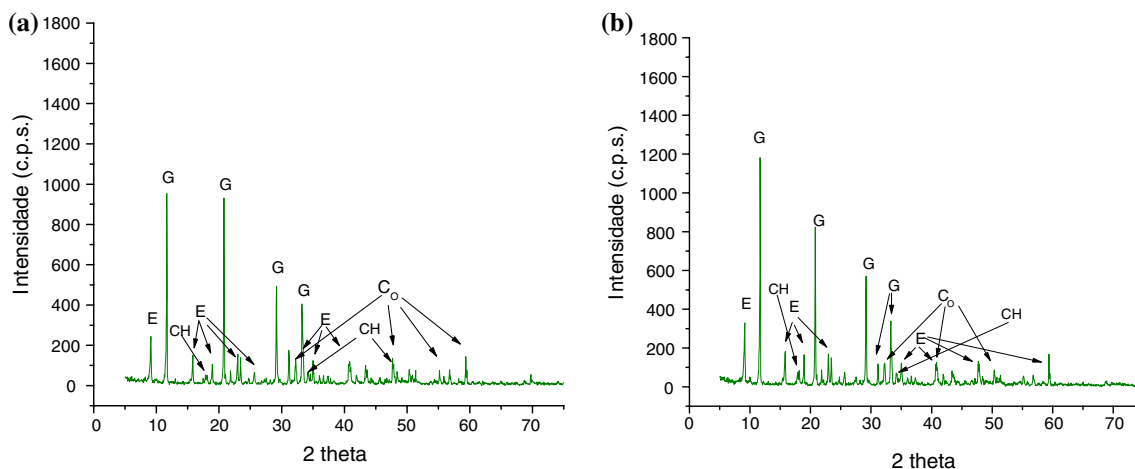


Fig. 9 XRD patterns recorded from the hydrated pastes at 7 days (a) and 14 days (b). Key: E = ettringite; G = gypsum; C_o = orthorhombic C_3A ; CH = calcium hydroxide

the paste—in this study by adding lime to the mixture—the normal dissolution rate of C_3A does not occur and, consequently, inhibits the formation of ettringite.

Another factor to consider is the difference between the crystalline structures of cubic and orthorhombic sample. Orthorhombic C_3A lends itself to selective removal of Na

from its structure, creating two zones of attack; a surface layer or zone that is enriched in Al, relative to the bulk composition and, at greater depth, a zone whereby Ca and Al remain, but from which Na is actively removed by selective hydrolysis [22]. This selective removal explains the shorter reaction time of the orthorhombic C_3A ; the

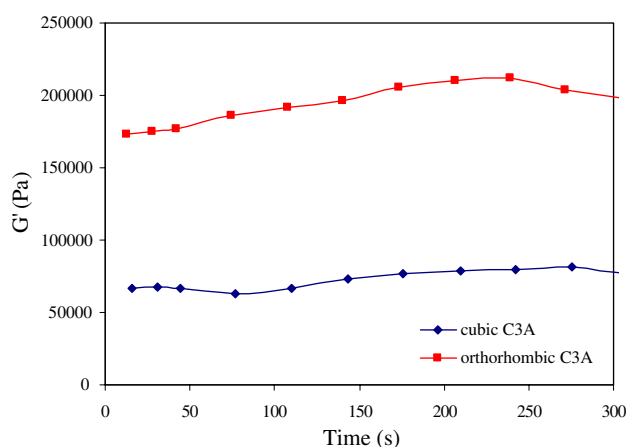


Fig. 10 Storage modulus (G') of cubic and orthorhombic C_3A mixed with gypsum (C_3A :gypsum—1:1.9). $w/s = 0.6$

relatively easy dissolution of the protective layer of the grain leads to a faster formation of ettringite.

High alkali contents in the clinker phase increase the pH of cement paste, which, because of the common ion effect, decrease the calcium concentration in solution and also promote the dissolution of C_3A [23]. Based on the results of this study, the high alkali (Na-doped C_3A) content accelerates hydration and the set of the mix. Most of the literature acknowledges that alkalis accelerate early hydration and also increase early strength, which explains the faster hydration of orthorhombic C_3A at early ages noted on the rheometric measurements. Conversely, it is generally accepted that alkalis decrease strength at 28 days and later [23–25]. Further research is necessary to explain this apparent contradiction.

Conclusions

An analysis of the hydration of cubic and orthorhombic C_3A by FE-SEM and X-ray diffraction (XRD) demonstrated:

- based on the size and consumption of C_3A and gypsum on these pastes the orthorhombic C_3A + gypsum presented a faster rate of formation of ettringite crystals, which were also longer;
- based on the influence of lime on these aluminates hydration, in the orthorhombic C_3A paste, the ettringite formation seems to be more retarded. Likewise, the size of ettringite crystals seems to be smaller when compared with the correlated orthorhombic C_3A paste with no lime;
- no monosulfoaluminate formation was observed.

Rheometric measurements showed that orthorhombic C_3A mixes presented higher increase in stiffness than cubic

C_3A at very early stages of hydration. Thus, this crystalline form of Na-doped C_3A (orthorhombic), when present in high amounts in the clinker, may cause problems with setting time and workability.

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